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# **Eu(III)-FULVIC ACID COMPLEXATION: EVIDENCE OF FULVIC ACID CONCENTRATION DEPENDENT INTERACTIONS BY TIME-RESOLVED LUMINESCENCE SPECTROSCOPY.**

Y.Z. KOUHAIL, M.F. BENEDETTI, AND P.E. REILLER

ABSTRACT: Europium speciation is investigated by time-resolved luminescence spectroscopy (TRLS) in the presence of Suwannee River fulvic acid (SRFA). From complexation isotherms built at different total Eu(III) concentrations, pH values, ionic strength, and SRFA concentrations, it appears that two luminescence behaviors of Eu(III) are occurring. The first part, at the lowest  $C_{\text{SRFA}}$  values, is showing the typical luminescence evolution of Eu(III) complexed by humic substances—*i.e.* the increase of the asymmetry ratio between the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transitions up to a plateau—, and the occurrence of a bi-exponential decay—the first decay being faster than free  $\text{Eu}^{3+}$ . At higher  $C_{\text{SRFA}}$ , a second luminescence mode is detected as the asymmetry ratio is increasing again after the previous plateau, and could correspond to the formation of another type of complex, and/or it can reflect a different spatial organization of complexed europium within the SRFA structure. The luminescence decay keeps on evolving but link to hydration number is not straightforward due to quenching mechanisms. The Eu(III) chemical environment evolution with  $C_{\text{SRFA}}$  is also ionic strength dependent. These observations suggest that in addition to short range interactions—intra-particulate complexation—, there might be interactions at longer range—inter-particulate repulsion—between particles that are complexing Eu(III) at high  $C_{\text{SRFA}}$ . These interactions are not yet accounted by the different complexation models.

## **1. INTRODUCTION**

The use of rare earths, and particularly the lanthanides (Ln), is increasing in modern industry.<sup>1</sup> Their importance in the understanding of geochemical processes, the presence of radioisotopes of lanthanides in spent nuclear fuels and radioactive wastes, and their analogy with some actinides (An) under the +III oxidation state, justify a better understanding of their environmental chemistry in waters, soils, and sediments.

Humic substances (HS), mainly composed of humic (HA) and fulvic (FA) acids are one of the main component of aquatic and soil ecosystems and are known to play an important role in the binding and transport of trace metals such as Ln(III).<sup>2-4</sup> Because of their strong interactions with surfaces<sup>5</sup> and their colloidal properties,<sup>6</sup> HS may affect Ln(III) either by supporting their mobility in water, or by limiting their migration in soils and sediments.

HS contain a great diversity of binding sites making it difficult to define equilibrium constants for each complexation reaction. This has led to a wide variety of models.<sup>7</sup> The most advanced models that permit to account for heterogeneity of HS, metal loading, pH, and ionic strength effects consider HS either as a mixture of discrete groups of sites—with different degree of correlations between these groups of sites—, *e.g.*, Model VI-VII,<sup>8,9</sup> or as a continuous distribution of groups of sites, *e.g.*, NICA-Donnan.<sup>10</sup> These kinds of models consider electrostatic phenomena, but the descriptions are somewhat different—hard sphere with a Donnan potential at the interface *vs.* permeable Donnan gel, respectively—when the structure of HS in general, and the structure of the Ln(III)-HS complexes in particular, remains largely under discussion.

Some Ln(III) and An(III) show a remarkable luminescence that is linked both to symmetry of their chemical environment,<sup>11</sup> and to the amount of water molecules in the first hydration sphere.<sup>12,13</sup> This information can be obtained both from the evolution of the luminescence spectrum and from the decay time. This has been the basis of a vast literature on the interaction between Ln-An(III) and HS.<sup>14-27</sup> Particularly, it has been shown that coordination structure around a metal ion is continuously modified by HS complexation when pH is varying.<sup>20,28</sup> Time resolution of the luminescence signal, through time-resolved luminescence spectroscopy (TRLS), was used to obtain complexation constants as well as structural properties.

The complexation strength of Ln(III) by HS can be considered relatively homogeneous within the series,<sup>29-31</sup> in agreement with the strong proportion of oxygen containing functionalities of HS.<sup>30,32</sup> Milne et al.<sup>33,34</sup> proposed generic complexation data for Ln(III) and An(III) in the framework of the NICA-Donnan model, but the great diversity of the reported studies, and the inherent heterogeneity of the different HS samples used throughout these studies led to some problems, particularly the proposed parameters for An(III), but also between Ln(III). As an example, Milne et al.<sup>34</sup> proposed different median affinity constants,  $\log_{10} \tilde{K}_{M^{n+},i}$ , for Am(III) and Cm(III), which is relatively surprising knowing the strong analogy between these two actinides(III), particularly regarding HS interactions.<sup>18</sup> The correlation between NICA-Donnan parameters—Figure 1 of Milne et al.<sup>34</sup>—and the first hydrolysis constants of the metals,  $\log_{10} {}^*\beta_1^{\circ}$ , also exemplify this problem: Am(III) and Cm(III) are supposed to have comparable  $\log_{10} {}^*\beta_1^{\circ} \approx -7$ ,<sup>35</sup> when Am(III) appears close to  $\text{UO}_2^{2+}$ — $\log_{10} {}^*\beta_1^{\circ}$  *viz.* -5.8 in Figure 1 of Milne et al.<sup>34</sup> and  $\log_{10} {}^*\beta_1^{\circ} = -5.25$  in Guillaumont et al.<sup>35</sup> Furthermore, the particular interaction of HS with metals *vs.* pH,  $\text{CO}_3^{2-}$  and oxalate concentration, etc., led to the proposition of the formation of ternary complexes,<sup>20,36-40</sup> which are not always necessary to interpret

experimental data within the framework of NICA-Donnan<sup>23,25,41</sup> or Model VI-VII,<sup>42-44</sup> but was sometimes proposed nevertheless.<sup>39,40</sup>

Cations are able to bridge two different polymer molecules,<sup>45</sup> and this supramolecular association increases with cation valence.<sup>46</sup> Supramolecular associations of HS are also known.<sup>47</sup> The effect of cations on these supramolecular structures was suggested<sup>48</sup> but needs further works.<sup>49-52</sup> Nevertheless, the effect of Eu(III) on the aggregation of HA was shown,<sup>53-55</sup> but the effect of HS concentration received little attention. There is therefore still a need for systematic studies of Ln(III)-HS complexation at varying pH, HS concentration, and ionic strength with spectroscopic information on the chemical environment of the metal.

Our aim is to propose an as comprehensive as possible study of the speciation of a trivalent luminescent lanthanide, Eu(III), in a wide parametric space in term of pH values, ionic strength, and HS concentration to better understand Ln(III)-NOM interactions and structures of NOM complexes with these trivalent cations. Time-resolved luminescence spectroscopy could be a useful tool to evidence the effect of the supramolecular structures on Eu(III)-NOM complexes since it provides information on Eu(III) environment. We will use the Suwannee River fulvic acid (SRFA), considered as a proxy of natural organic matter reactivity,<sup>56</sup> the relatively low UV-Visible absorption properties of which permits to use rather high concentration of FA in TRLS experiments compared to other HS extracts.<sup>24</sup> We will take advantage of the luminescence properties of Eu(III) to characterize the Eu(III)-FA complexation and to evaluate its chemical environment using TRLS.

## 2. MATERIALS AND METHODS

### 2.1. REAGENTS AND CHEMICALS

Europium(III) stock solution ( $10^{-4}$  mol/L) is obtained from the dissolution of  $\text{Eu}_2\text{O}_3$  (Johnson Matthey, 99.99%) in  $\text{HClO}_4$ . All solutions are prepared using milli-Q water from a Direct Q3 Millipore. Suwannee river fulvic acid (2S101F) is purchased from the International Humic Substances Society and used as received. The ionic strength is fixed with  $\text{NaClO}_4$  (Sigma Aldrich, >98%) at 0.02 M, 0.1 M and 0.5 M. The pH values are fixed at 4, 6, and 7 by the addition of small amounts of freshly prepared 0.1 M NaOH and/or  $\text{HClO}_4$ . Measurements are done using a pH meter Seven Easy (Mettler Toledo) with a combined glass electrode Inlab micro, filled with  $\text{NaClO}_4$  3M to avoid  $\text{KClO}_4$  precipitation in the frit of the electrode with the original KCl filling. The electrode signal in mV is calibrated using commercial buffer solutions (pH 4.01, 7.01, and 10.00).

## 2.2. TIME-RESOLVED LUMINESCENCE SPECTROSCOPY

The experimental set-up and luminescence decay times fitting have already been described elsewhere.<sup>5,24,26,28</sup> The 600 lines.mm<sup>-1</sup> grating of the Acton spectrometer (slit 1 mm) is used. The luminescence signal is collected during a gate width ( $W$ ) of 300  $\mu$ s, at a gate delay ( $D$ ) of 10  $\mu$ s after the excitation by the laser flash. To increase the signal to noise ratio, 1,000 to 10,000 accumulations are performed for each spectrum, the background noise is subtracted, and the luminescence is divided by the average of 100 laser shots energy before and after the acquisition, and by the number of acquisitions (accumulations).

Because of the weak energy received by the system during the experiments, photochemical reactions of humic substances<sup>57</sup> can be excluded. The excitation wavelength is set at  $\lambda_{\text{exc}} = 393.7$  nm, with an energy typically less than 2 mJ, which corresponds to the  $^5L_6 \leftarrow ^7F_0$  transition of Eu(III). After inner conversion, the observed luminescence corresponds to the transitions from the  $^5D_0$  excited state to the ground  $^7F_j$  manifold.<sup>58</sup> We focus our attention on three transitions: the  $^5D_0 \rightarrow ^7F_0$  transition ( $\lambda_{\text{max}} = 578.8$  nm), forbidden by the selection rules but apparent when Eu(III) chemical environment loses its centro-symmetry; the  $^5D_0 \rightarrow ^7F_1$  transition ( $\lambda_{\text{max}} = 591.1$  nm), a magnetic dipole transition; and the  $^5D_0 \rightarrow ^7F_2$  electric dipole transition ( $\lambda_{\text{max}} = 615.1$  nm), which is very sensitive to europium speciation,<sup>59</sup> and known as a hypersensitive transition. The peak area ratio between the  $^5D_0 \rightarrow ^7F_2$  and the  $^5D_0 \rightarrow ^7F_1$  transitions, hereafter referred as the asymmetry ratio  $^7F_2/^7F_1$ , has often been used to estimate complexation constants,<sup>60</sup> and structural modifications.<sup>5</sup>

## 2.3. MODELING

Modeling of Eu-SRFA interactions is performed using ECOSAT software,<sup>61</sup> which includes speciation with inorganic ligands and humic substances through the NICA-Donnan model.<sup>10</sup> It merges the Non-Ideal Competitive Adsorption (NICA) model with a continuous distribution of sites, and a Donnan potential description to account for electrostatic interactions within the structure of HS considered as a water-permeable gel. The model accounts for electrostatic interactions,<sup>62</sup> sites heterogeneity, non-ideality of the metal-HS complexation, and competition between metals. Milne et al. proposed generic data for HA and FA complexation with protons,<sup>33</sup> and several metals of interest, including Ln(III) and An(III).<sup>34</sup> The inorganic side reactions of Eu(III) with OH<sup>-</sup> are implemented in the ECOSAT database.<sup>63</sup>

Site densities of the two distribution of sites of SRFA— $Q_{max,1}$ , and  $Q_{max,2}$ —, parameters representing the intrinsic heterogeneity—widths of the distributions of sites  $p_1$  and  $p_2$ —, and generic proton parameters—non-ideality parameter  $m_{H^+,i}$  and median affinity constant  $\log_{10}\tilde{K}_{H^+,i}$ —for low-affinity type of sites—so-called carboxylic  $S_1$ —and high-affinity type of sites—so-called phenolic  $S_2$ —proposed by Milne et al.<sup>33,34</sup> are recalled in Table S1 of the Supporting Information (SI).

### 3. RESULTS AND DISCUSSION

#### 3.1. SPECTROSCOPIC DATA

Eu(III) speciation is first studied at fixed pH values of 4, 6, and 7, fixed ionic strength of 0.1 M, and at varying  $C_{Eu(III)}$ —0.5, 1, and 10  $\mu\text{M}$ —and SRFA concentrations—from 0 to 2,8  $\text{g}_{\text{SRFA}}/\text{L}$ . The obtained luminescence spectra shown in Figure S1 of the SI are normalized to the peak area of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition. The complexation of Eu(III) in the system is evidenced by the increase of both the forbidden  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  and the hypersensitive  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions. The  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition appears at pH above 5 in the absence of SRFA, or in the presence of a slight amount of SRFA at whatever pH value. This typically indicates a loss of centro-symmetry compared to the aquo-complex  $\text{Eu}(\text{H}_2\text{O})_n^{3+}$  and the formation of  $\text{Eu}(\text{OH})_n^{(3-n)+}$ —minor under these pH conditions—and Eu(III)-SRFA complexes.

The  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition relative intensity is increasing with complexation<sup>59</sup>—here with SRFA concentration—and shows a narrowing with metal complexation and a shift toward lower wavelengths (see Figure S1 of the SI). The variation of the relative intensity of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  area to the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  area with  $C_{\text{SRFA}}$ , provides information on Eu(III) chemical environment. It is then possible to use this evolution as a spectral titration curve.<sup>60</sup>

The evolutions of the asymmetry ratio  $^7\text{F}_2/^7\text{F}_1$  *vs.*  $C_{\text{SRFA}}$  at different pH values,  $C_{\text{Eu(III)}}$  (Figure 1) are showing unusual features. Two different Eu(III) luminescence behaviors are evidenced. First, the peak area ratio shows an increase with  $C_{\text{SRFA}}$  values— $C_{\text{SRFA}} < 100 \text{ mg}_{\text{SRFA}}/\text{L}$  at pH 4,  $C_{\text{SRFA}} < 40 \text{ mg}_{\text{SRFA}}/\text{L}$  at pH 6, and  $C_{\text{SRFA}} < 20 \text{ mg}_{\text{SRFA}}/\text{L}$  at pH 7—until a plateau seems to be reached. This evolution reflects the typical luminescence evolution of Eu(III) complexed by organic compounds.<sup>5,64-66</sup> Second, after the plateau the asymmetry ratio keeps on increasing with  $C_{\text{SRFA}}$ . Chung et al.<sup>21</sup> reported a decrease in the asymmetry ratio after the plateau with increasing  $C_{\text{Eu(III)}}$  in the case of a soil FA, but we interpret this evolution as the saturation of their humic extracts and the increase of the proportion of free Eu in the system.

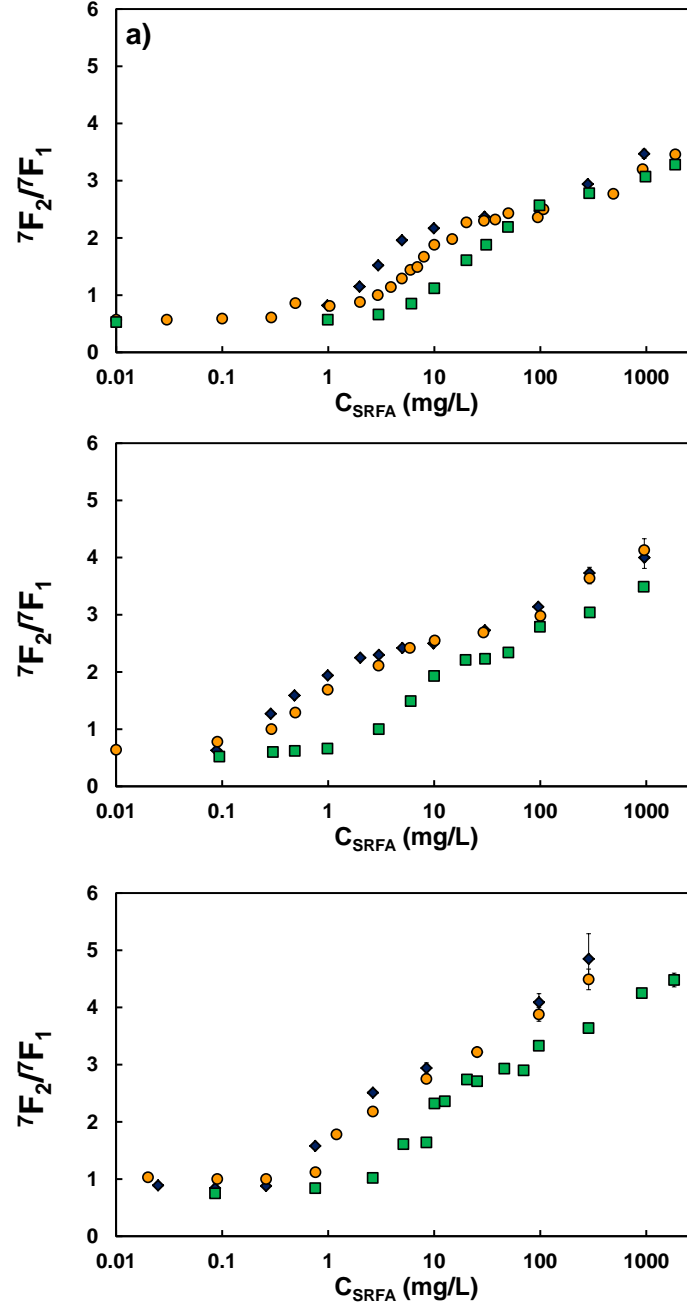


Figure 1. Evolution of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  area ratios *vs.*  $C_{\text{SRFA}}$  at  $I = 0.1$  M, pH 4 (a); pH 6 (b), and pH 7 (c) for  $C_{\text{Eu(III)}}$  of 0.5 (blue diamonds), 1 (orange circles), and 10  $\mu\text{M}$  (green squares):  $\lambda_{\text{exc}} = 393.7$  nm,  $D = 10$   $\mu\text{s}$ ,  $W = 300$   $\mu\text{s}$ , 600 lines. $\text{mm}^{-1}$  grating. Error bars represent  $2\sigma$  of the area ratio using the trapezoid method.

## 3.2. DECAY TIME EVOLUTIONS

Eu(III) luminescence decay times were measured with an initial delay  $D = 10 \mu\text{s}$ , a gate step of  $15 \mu\text{s}$ , and a gate width  $W = 300 \mu\text{s}$  for  $C_{\text{Eu(III)}}$  of  $1 \mu\text{M}$  and  $10 \mu\text{M}$  at pH 4, 6 and 7 (Figure S2 of the SI)—the signal at  $C_{\text{Eu(III)}} = 0.5 \mu\text{M}$  being too weak to obtain a reliable decay time analysis.

At pH 4 (Figure S2a of the SI), Eu(III) is showing a mono-exponential decay up  $2.98 \text{ mg}_{\text{SRFA}}/\text{L}$ . The  $\tau$  values do not differ from the free  $\text{Eu}^{3+}$  one, *i.e.*  $\tau = 110 \mu\text{s}$ .<sup>12,13</sup> For  $C_{\text{SRFA}}$  higher than  $2.98 \text{ mg}/\text{L}$ , bi-exponential decays are obtained, which could be attributed to the presence of two radiative decay processes linked to two different excited species.<sup>26</sup> The first decay  $\tau_1$  is faster than free  $\text{Eu}^{3+}$ , and does not seem to vary strongly with SRFA concentration.<sup>5,28</sup> The relationships that links the hydration number cannot be applied, as in the case of benzoic acids.<sup>64,66-68</sup> The second decay,  $\tau_2$ , is slower than free  $\text{Eu}^{3+}$ , and is showing two different comportments as a function of  $C_{\text{Eu(III)}}$ . From  $2.98$  up to *ca.*  $100 \text{ mg}_{\text{SRFA}}/\text{L}$ —*i.e.*, the  $C_{\text{SRFA}}$  value where all the  ${}^7\text{F}_1/{}^7\text{F}_2$  evolution are merging in Figure 1—, the  $\tau_2$  value is increasing up to *ca.*  $180 \mu\text{s}$  whatever the  $C_{\text{Eu(III)}}$ . This is the typical comportment of Eu(III) complexed by HS, which can be interpreted as the substitution of inner-sphere water molecules by SRFA functionalities. The  $\tau_2$  value *ca.*  $175 \mu\text{s}$  is in agreement with the evolution observed for Eu-HS complexes.<sup>24</sup> The application of the relationship from Kimura and Choppin<sup>13</sup> is debatable, but would indicate the loss of *ca.*  $3.6 \pm 0.5$  water molecules. At higher  $C_{\text{SRFA}}$  values, the decay time evolutions are more intricate to interpret. If  $\tau_2$  values keep on increasing for  $C_{\text{Eu(III)}} = 1 \mu\text{M}$ —*i.e.*,  $\tau_2$  *ca.*  $235 \mu\text{s}$  and a loss of *ca.*  $5.2 \pm 0.5$  water molecules— they also seem to attain a plateau. Conversely,  $\tau_2$  seems to decrease for  $C_{\text{Eu(III)}} = 10 \mu\text{M}$ . The application of the relationship from Kimura and Choppin<sup>13</sup> has no sense here as it would indicate a “gain” of *ca.*  $1.4 \pm 0.5$  water molecules between  $100$  and  $1000 \text{ mg}_{\text{SRFA}}/\text{L}$ , when the increases in both  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  area and asymmetry ratio (Figure 1) indicate a continuing change in the complexation environment of Eu(III). The combination of the apparent plateau for  $C_{\text{Eu(III)}} = 1 \mu\text{M}$  and the decrease at  $10 \mu\text{M}$ , may lead to a possible dynamic quenching, the origin of which is not possible to determine and would require further investigations.

At pH 6 (Figure S2b of the SI), only mono-exponential decays can be fitted for  $C_{\text{SRFA}}$  lower than  $30 \text{ mg}/\text{L}$ . There is only a very slight increase in the  $\tau$  values from *ca.*  $100$  to *ca.*  $140 \mu\text{s}$ —loss of *ca.*  $2.2 \pm 0.5$  water molecules. Bi-exponential decays are obtained for  $C_{\text{SRFA}}$  higher than  $30 \text{ mg}_{\text{SRFA}}/\text{L}$  for  $C_{\text{Eu(III)}}$  of  $1$  and  $10 \mu\text{M}$  up to  $1 \text{ g}_{\text{SRFA}}/\text{L}$ . One also note the difference between  $C_{\text{Eu(III)}}$ , which is



reminiscent of the evolution at pH 4 and would also indicate a quenching mechanism. The final situation at  $C_{\text{Eu(III)}}$  and  $C_{\text{SRFA}} = 1 \text{ g}_{\text{SRFA}}/\text{L}$  would indicate the loss of  $\approx 5.8 \pm 0.5$  water molecules.

At pH 7 (Figure S2c of the SI), mono-exponential decays are first obtained at lower  $C_{\text{SRFA}}$ . Bi-exponential decays are obtained for  $C_{\text{SRFA}}$  higher than  $3 \text{ mg}_{\text{SRFA}}/\text{L}$  for  $C_{\text{Eu(III)}}$  of 1 and  $10 \mu\text{M}$ . The obtained decays are showing a slight increase in  $\tau_1$  and a stronger continuous increase in  $\tau_2$  up to  $285 \mu\text{s}$  for  $C_{\text{Eu(III)}} = 10 \mu\text{M}$ —loss of  $\approx 6.0 \pm 0.5$  water molecules. Both Eu(III) concentration seem to follow the same trend even if the  $\tau_2$  value for  $C_{\text{Eu(III)}} = 10 \mu\text{M}$  and  $C_{\text{SRFA}} = 1 \text{ g}_{\text{SRFA}}/\text{L}$  is clearly below the trend. The possible quenching mechanism seems to be less operant here.

Nevertheless, the decay time evolutions seem to confirm that different environments are present at different  $C_{\text{SRFA}}$ . The estimation of hydration sphere here is constrained by the relationship from Kimura and Choppin<sup>13</sup>, the validity of which has not been demonstrated up to now in these systems.

### 3.3. EFFECT OF IONIC STRENGTH.

In order to improve the understanding of the second mode in the complexation isotherms, we performed experiments at pH 7 and various ionic strengths ( $I = 0.02, 0.1$ , and  $0.5 \text{ M NaClO}_4$ ), which asymmetry ratios' evolutions are shown in Figure 2. First, before the plateau, *i.e.*,  $< 10 \text{ mg}_{\text{SRFA}}/\text{L}$ , the complexation is decreasing as expected with ionic strength,<sup>10,69</sup> whilst a reverse influence is shown at higher  $C_{\text{SRFA}}$ . This second part, where the peak area ratio is still increasing, means that the chemical environment of Eu(III) is ionic strength dependent. If one considers that the decrease of the asymmetry ratio with ionic strength at low  $C_{\text{SRFA}}$  indicates a typical weaker binding,<sup>18,69,70</sup> then one can also consider that the increase in asymmetry ratio at higher  $C_{\text{SRFA}}$  with ionic strength indicates a stronger binding environment. This was never reported in previous studies focusing on metal-organic matter speciation.<sup>24</sup>

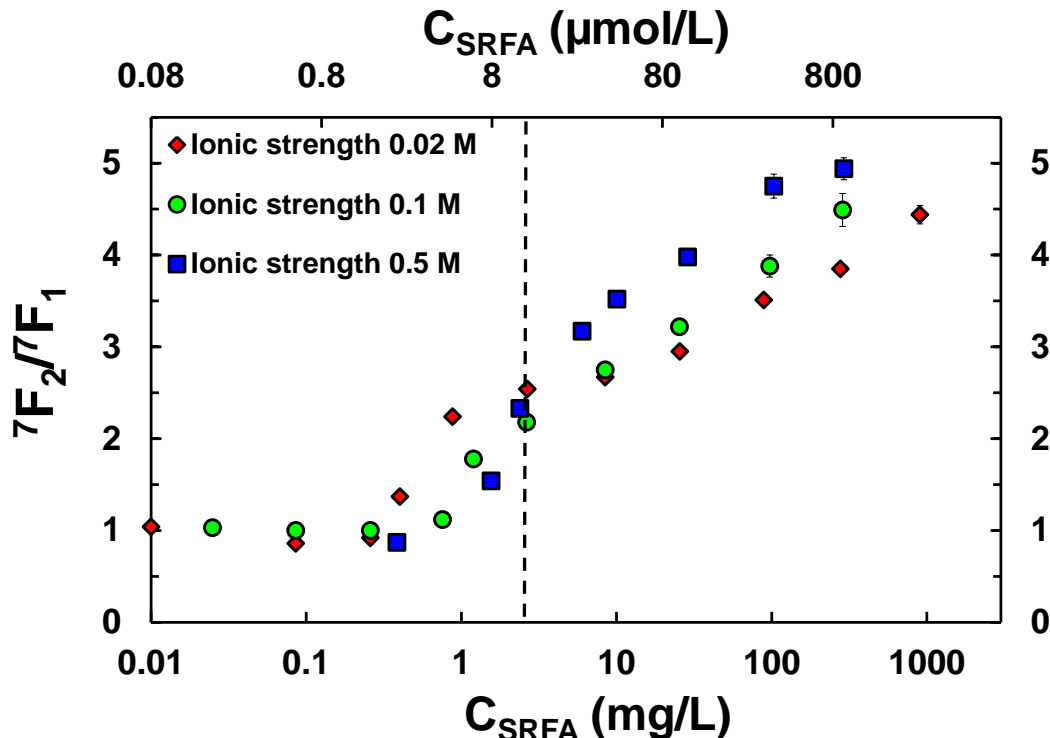


Figure 2. Evolution of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  area ratios vs.  $C_{\text{SRFA}}$  the ionic strength ( $I = 0.02 \text{ M}$ , red diamonds;  $I = 0.1 \text{ M}$ , green circles;  $I = 0.5 \text{ M}$ , blue squares) at  $C_{\text{Eu(III)}}$  of  $1 \mu\text{M}$  and pH 7. Dashed line corresponds to the inversion of the ionic strength trend.

### 3.4. SIMULATION AND MODELING.

For a better understanding of the second mode in complexation isotherms, simulations of Eu(III)-SRFA complexation are done using NICA-Donnan generic parameters<sup>34</sup> for  $C_{\text{Eu(III)}}$  of 0.5, 1 and  $10 \mu\text{M}$ , at  $I = 0.1 \text{ M}$  (Figure S3 of the SI). Eu(III) is increasingly fixed to SRFA, mostly to  $S_1$  sites at pH 4. The proportion of Eu(III) bound to  $S_2$  sites is increasing with pH. The total complexation is expected around  $C_{\text{SRFA}} = 100 \text{ mg}_{\text{SRFA}}/\text{L}$  for pH 4,  $C_{\text{SRFA}} = 40 \text{ mg}_{\text{SRFA}}/\text{L}$  for pH 6, and  $C_{\text{SRFA}} = 20 \text{ mg}_{\text{SRFA}}/\text{L}$  for pH 7. No account for mixed  $\text{Eu}(\text{OH})_n\text{FA}$  complexes is needed in these simulations *vs.* pH. Nevertheless, it can be recalled that mixed  $\text{Fe}(\text{OH})\text{HA}$ , and  $\text{Al}(\text{OH})\text{HA}$  complexes was proposed in the framework of NICA-Donnan<sup>40</sup> or Model VI,<sup>39</sup> respectively. No further modification of the speciation is expected from the calculation at higher  $C_{\text{SRFA}}$ . Therefore, the further increase of asymmetry ratio should correspond to another complexation/fixation mode not accounted for by any available model, yet.

It is then possible to compare our dataset to the prediction of the NICA-Donnan model. First, the asymmetry ratios are used as indicators of the proportion of Eu(III) complexed to SRFA (Figure S4 of the SI).<sup>60</sup> The asymmetry ratio evolves with the metal to SRFA concentration ratio. When SRFA is not present in the system, the asymmetry ratio is the one for the Eu(III) aquo-complex. When the asymmetry ratio is reaching a plateau at pH 4 (Figure S4 of the SI), this suggests that all of Eu(III) is complexed to SRFA. This evolution is used as a spectral titration curve to calculate proportions of Eu(III) bound to SRFA (Figure 3a).<sup>60</sup> At pH 6, the existence of a plateau is less clear (Figure 1b) but seems to occur for  $C_{\text{SRFA}}$  of 10 mg<sub>SRFA</sub>/L for  $C_{\text{Eu(III)}}$  of 0.5  $\mu\text{M}$  and 1  $\mu\text{M}$ , and for  $C_{\text{SRFA}}$  of 30 mg<sub>SRFA</sub>/L for  $C_{\text{Eu(III)}}$  of 10  $\mu\text{M}$ . These values are supported by our previous simulations (*vide supra*, Figure S3 of the SI). At pH 6, Eu(III) is totally bound to the SRFA for concentrations *ca.* 10 mg<sub>SRFA</sub>/L for  $C_{\text{Eu(III)}}$  of 0.5  $\mu\text{M}$ , and 1  $\mu\text{M}$ , and for concentration *ca.* 30 mg<sub>SRFA</sub>/L for  $C_{\text{Eu(III)}}$  of 10  $\mu\text{M}$ . At pH 7 (Figure 1c), the end of the first complexation mode is set as for pH 6, when Eu(III) is fully bound to SRFA in our previous simulations, for concentrations of 2.6 mg<sub>SRFA</sub>/L for  $C_{\text{Eu(III)}}$  of 0.5 and 1  $\mu\text{M}$  and 10 mg<sub>SRFA</sub>/L for  $C_{\text{Eu(III)}}$  of 10  $\mu\text{M}$ .

For a better fit, NICA-Donnan parameters for Eu(III)-SRFA binding are adjusted. The adjustment of Eu(III) binding parameters for  $S_1$  sites is done at pH 4 only, because at higher pH values, due the presence of hydrolyzed species of Eu(III), the asymmetry ratio at low SFRA concentration could not correspond to free  $\text{Eu}^{3+}$ . Thus, the adjusted parameters for the low proton affinity sites  $S_1$  at pH 4 are used at pH 6 and 7 to adjust the parameters for the high proton affinity sites  $S_2$ .

The proportion of Eu(III)-SRFA complex for  $C_{\text{Eu(III)}}$  of 0.5, 1, and 10  $\mu\text{M}$  at pH 4, 6, and 7, and the modeling of Eu(III) bound to SRFA are shown in Figure 3. NICA-Donnan parameters for proton and Eu(III) binding to SRFA used in the model are presented in Table S1 of the SI. The model is slightly underestimating the complexation for  $C_{\text{Eu(III)}} = 0.5 \mu\text{M}$  at pH 4, but it is still in fair agreement with experimental data. It is worthy to notice in Table S1 of the SI that compared to generic parameters, Eu(III) complexation by SRFA is less important—lower  $\log_{10} \tilde{K}_{\text{Eu}^{3+},1}$ — and the distribution is more heterogeneous for  $S_1$  sites—lower  $n_{\text{Eu}^{3+},1}$ —, and that the complexation is stronger and less heterogeneous for  $S_2$  sites—higher  $\log_{10} \tilde{K}_{\text{Eu}^{3+},2}$ , and higher  $n_{\text{Eu}^{3+},2}$ . Milne et al.<sup>34</sup> proposed correlation between  $n_{\text{M}^{n+},i}$  and  $n_{\text{M}^{n+},i} \times \log_{10} \tilde{K}_{\text{M}^{n+},i}$  *vs.*  $\log_{10}^* \beta_1^\circ$ . As it can be anticipated from the very little difference between the simulations using generic parameters<sup>34</sup> and the modeling of our data, it can be seen in Table S1 of the SI that  $n_{\text{Eu}^{3+},1} \times \log_{10} \tilde{K}_{\text{Eu}^{3+},1}$  are in good agreement. Nevertheless,

it seems that  $n_{\text{Eu}^{3+},2} \times \log_{10} \tilde{K}_{\text{Eu}^{3+},2}$  is higher in our case leading to a slightly higher complexation than anticipated.

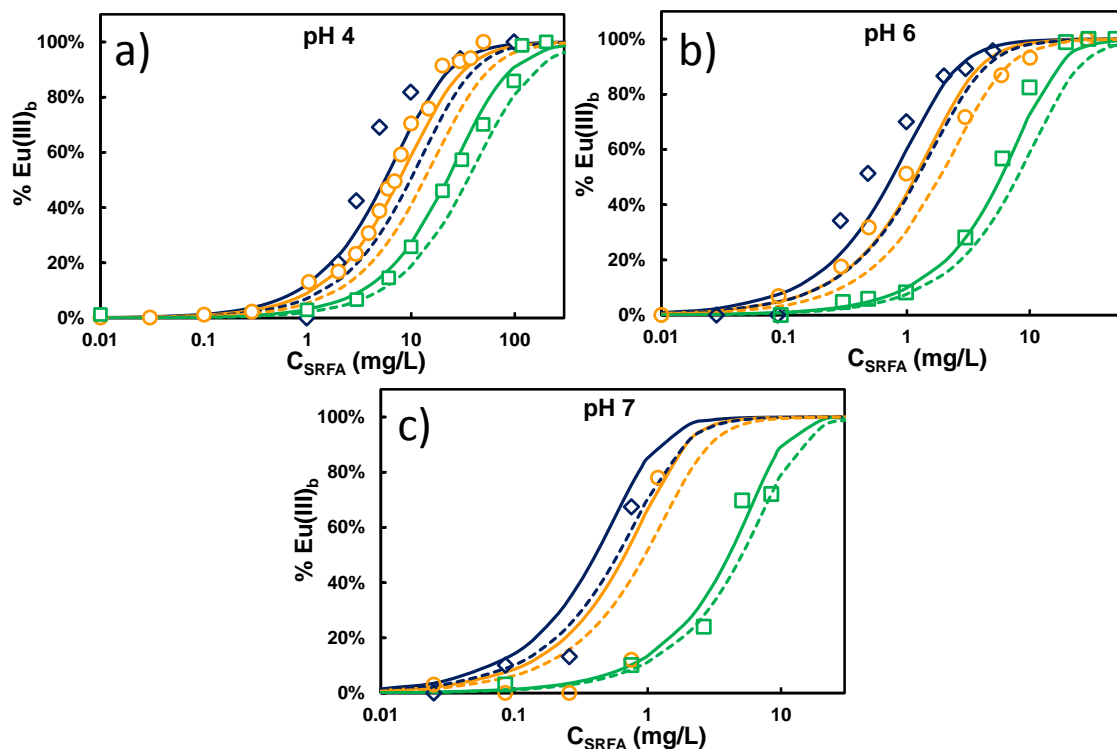


Figure 3. Proportion of Eu(III) bound to SRFA for Eu(III) concentrations of 0.5  $\mu\text{M}$  (blue diamonds), 1  $\mu\text{M}$  (orange circles) and 10  $\mu\text{M}$  (green squares) at pH 4 (a), 6 (b), and 7 (c). The dashed lines are the simulations and the solid lines are the results of our modeling of Eu(III) bound to SRFA. Adjusted and generic NICA Donnan parameters are given in Table S1 of the SI.

### 3.5. Eu(III)-SRFA INTERACTIONS.

It was possible to satisfactorily describe Eu(III)-SRFA interactions that occur in the first parts of the isotherms with the NICA-Donnan model. The increase in asymmetry ratio at higher  $C_{\text{SRFA}}$  with ionic strength (Figure 2), which indicates a change in the complexation environment, still needs to be cleared. The influence of varying metal concentration with constant HS concentration—see Hummel et al.<sup>70</sup> and references therein—is directly accounted for within the NICA-Donnan model,<sup>71</sup> and is not in play here. Assumptions are made, which may not necessarily exclude each other, regarding this original asymmetry ratio evolution at the higher  $C_{\text{SRFA}}$ : (i) it may correspond to the formation of another type of complex, *e.g.*, strong sites *vs.* weak sites or a 1:2 complex<sup>72-74</sup>; (ii) and/or

it can reflect a different spatial organization of the complexed europium constrained by a change in the SRFA structure. As the UV-Visible absorption of HS decreases rather monotonously with wavelength, one may also propose higher auto absorption of the  $^5D_0 \rightarrow ^7F_1$  transition wavelength span compared to the  $^5D_0 \rightarrow ^7F_2$  transition one with  $C_{\text{SRFA}}$ . The fact that the second increase occurs at lower  $C_{\text{SRFA}}$  with pH permits to exclude this hypothesis.

A possible explanation may rely in the influence of ionic strength on complexation and adsorption. Following the Debye-Hückel theory, the decrease in complexation with ionic strength at low  $C_{\text{SRFA}}$  is in line with the evolution of the activity coefficient with the reciprocal of the Debye length ( $\kappa$ ).<sup>75</sup> This indicates that at low  $C_{\text{SRFA}}$  the complexation occurs with rather isolated functional groups in the SRFA structure. At higher  $C_{\text{SRFA}}$  one can consider the interaction between SRFA entities as supramolecular associations of fulvic acid particles.<sup>47,49</sup> The variation of the hydrodynamic radius ( $R_H$ ) with ionic strength of the smallest entities of HS, including SRFA, has given contrasted results.<sup>76,77</sup> When d’Orlyé and Reiller<sup>77</sup> did not evidence a clear increase in  $R_H$  with ionic strength at pH 10 in Taylor dispersion analysis, Domingos et al.<sup>76</sup> reported a small decrease of diffusion coefficient of SRFA—small increase in  $R_H$ —with ionic strength between pH 2 and 8 in fluorescence correlation spectroscopy. This latter result was interpreted as a reduction of both intramolecular and intermolecular repulsion. Decreasing intramolecular repulsion will lead to molecular compression, while decreasing intermolecular repulsion can increase aggregation. It has also been shown that contrary to simple organics—and commonly to polyelectrolytes<sup>78,79</sup>—, adsorption of humic substances onto minerals is increasing with ionic strength.<sup>5,80</sup> Even if this effect is much weaker for FA compared to HA,<sup>81</sup> this means that HS entities in general can approach at shorter distances to each other in solution with increasing ionic strength. Following the Gouy-Chapman theory, Eu(III)-bearing SRFA entities can more easily approach each other with increasing ionic strength. The second part of the asymmetry ratio increase could therefore be due to the formation of complexes with higher stoichiometry between complexation sites that are not located on the same HS entity or “particle”. This suggests that there might be electrostatic driven interactions between fulvic acid sites in particles that are typically complexing Eu(III)—intra-particulate complexation mode—, and form Eu(III)-bridged complexes in the second part of the asymmetry ratio evolution—inter-particulate complexation mode. We can also notice that in complexation isotherms at pH 7 and various ionic strengths (Figure 2) the metal to ionized FA sites concentration ratio equals 10 at the boundary between the two-luminescence modes. In the second mode, we can assume that Eu(III)-bridged complexes are formed because of the decreasing metal to ionized FA sites concentration ratio.

The formation of 1:2 stoichiometry complexes was suggested by Bertha and Choppin<sup>73</sup> who studied interactions of HS (HA and FA) with Eu(III) and Am(III). Their results, using Schubert's method to determine binding constants, suggest the formation of 1:1 and 1:2 Eu-HS complexes from slope analyses of the variation of the distribution coefficient with humic acid concentration. At pH 4.5 Bertha and Choppin<sup>73</sup> proposed that Eu(III) is bound simultaneously by one or two carboxylate groups. In our study we could interpret our spectroscopically observed evolutions as the successive formation of the 1:1 and 1:2 Eu(III)-SRFA complexes. The ionic strength effect in complexation isotherms suggests that complexation sites may not be located on the same fulvic acid particle. Such interactions are not yet accounted for in any model describing metal-HS interactions, and would require either complete rewriting of the models, or adaptation of the existing models to this not yet noticed effect.

Within the NICA-Donnan model framework, the Donnan volume  $V_D$  is optimized to build the acid-base titration master curves. It decreases with ionic strength following an empirical relationship.<sup>62</sup> The Donnan potential  $\psi_D$  inside this volume is assumed negative and constant inside, and nil outside the particle—or water-permeable Donnan gel. It can be calculated from the ratio of the activity of ions inside and outside the Donnan gel, and from the charge density inside the gel, so that the decrease in complexation with ionic strength is linked to a decrease in the negative value of  $q/V_D$  and  $\psi_D$ .<sup>10</sup> One could then think that the increase of Eu(III) association at high  $C_{SRFA}$  with ionic strength could be linked to an apparent increase in the negative value  $q/V_D$  and  $\psi_D$ . The verification of this hypothesis implies the determination of the size of Eu(III)-SRFA complexes at varying pH, Eu and SRFA concentrations, and ionic strength. It is nevertheless, worthy to recall that, as already discussed in Benedetti *et al.*,<sup>62</sup> the Donnan model seems not to be very realistic for FA because the changes in Donnan volumes as a function of ionic strength are too large.

Another possibility is the account of an interfacial potential, as a double layer spreading outside the Donnan gel as proposed by Saito *et al.*,<sup>82,83</sup> which should be implemented to be effective at high  $C_{SRFA}$  and should mostly be ineffective at low  $C_{SRFA}$  in order to represent the already successful modeling obtained up to now within the framework of NICA-Donnan.

## SUPPORTING INFORMATION.

The supporting information contains four Figures and one Table. One Figure shows Eu(III)-SRFA normalized luminescence spectra to the  $^5D_0 \rightarrow ^7F_1$  transition at 0.1 M NaClO<sub>4</sub> and  $C_{Eu(III)} = 1$

$\mu\text{M}$  at pH 4, 6 and 7. One Figure shows luminescence decay times of Eu(III) at pH 4, 6 and 7 depending on fulvic concentration for Eu(III) concentrations of 1  $\mu\text{M}$  and 10  $\mu\text{M}$ . One Figure shows the simulation of Eu bound to SRFA and NICA-Donnan parameters using generic parameters. One Figure shows the transformation of asymmetry ration in proportion of Eu(III) bound to the fulvic acid. One Table is showing the NICA-Donnan generic parameters for simulation, and the NICA-Donnan parameters obtained from modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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